

# Estimation of selective reduction of iron and phosphorus from manganese ores of different genesis

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**Abstract.** The possibility of selective reduction of iron from complex oxides by carbon monoxide gas is investigated. Brazilian ore rich in manganese oxide, ferromanganese ore from the Selezenskoye Deposit (Russia) and concentrate from the Zhayrem GOK (Kazakhstan) were used as samples. Experiments have shown that it is possible to selectively reduce iron from complex manganese ores to a metallic state not only with solid carbon, but also with carbon monoxide. Experimental results of solid-phase reduction showed that at a temperature of 900 °C. With an exposure time of 1.5 hours, the release of metallic iron is detected. At the same time, in the atmosphere with the metal phase, there is no presence of other elements other than iron in the metal. As the temperature rises to 1000 °C, the amount of metallic iron, as well as manganese and phosphorus, increases. At a temperature of 1000 °C, phosphorus turns into metal, despite the type of reducing agent. In all experiments, oxides of manganese, silicon and calcium remained in the oxide part.

## 1. Introduction

The ferrous metallurgy is the major consumer of manganese products in the world. Approximately 95 % of all the manganese ore is consumed during production of steel, mostly in the form of ferromanganese or silicomanganese, as well as in the form of other small-scale production associated with ferroalloys [1–2]. In addition to the metallurgical sphere, manganese is also used in other industries [3–4].

The confirmed supply of manganese ores in the world is 3.5 billion tons and the total amount is estimated to be 8.9 billion tons [5]. The results of various studies of preliminary reduction of metals from iron [6–7], chromium [8–11], and also manganese ores [12–14] have been recently published. Currently, there are large reserves of low-quality ferromanganese ores in the CIS countries, which after processing can be considered as an alternative raw material base for manganese production. In Kazakhstan at the Western Kamys deposit the reserves of oxidized manganese ores are estimated to be 700–800 thousand tons [15], and most of this raw material base is represented by the ferromanganese ores. In addition to the ores of the Western Kamys deposit, iron-manganese ores are also found in other deposits of central Kazakhstan. This refers to the deposits, e. g. Zhomart, Kamys, and Eastern Karazhal. These deposits have large amount of manganese ores with a high iron content [16]. Based on the literature data [17], it can be concluded that Kazakhstan has huge reserves of manganese ores; however, these ores are not always suitable for production of standard grade manganese alloys and only about 70 % of them are ferromanganese grades of ore. The iron manganese ores of the Middle Obuzha are known in Ukraine [18]. On the territory of Russia [19] in the Kemerovo region there are



iron-manganese ores of the Durnovsky deposit containing about 300 thousand tons, as well as the Selezensky deposit, represented as rich boulder ores of manganese and fragments of iron-manganese ores; the estimated reserves are 5 million tons. Currently, there are no efficient processing methods for such ores. A distinctive feature of the ferromanganese ores is their high content of both manganese and iron-containing minerals. The technological schemes which are developed for the mechanical enrichment of this type of ore do not allow sufficient separation of minerals of iron and manganese. In work [15] the author's study made it possible to establish an approximate temperature for firing iron-manganese ores in the presence of carbon, which was estimated to be 800–900 K. In works [20–21] the authors studied the features of the hydrometallurgical processing of iron-manganese ores using advanced ferrous-sulfate technology. All of these methods for removal of phosphorus and iron from composition of the ferromanganese ores have not yet been implemented in practice. Therefore, the development of theory and technology of processing is required for processing of ferromanganese ores.

## 2. The aim of this work

Was a comparative assessment of the possibility of selective reduction of metals from manganese ores using solid carbon and gaseous carbon monoxide as reducing agents.

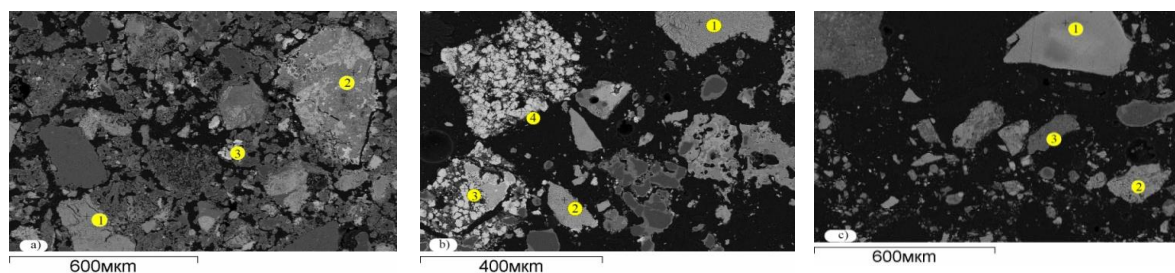
## 3. Materials and methods

Three samples were used as the studied material: Brazilian ore rich in manganese oxide, ferromanganese ore of the Selezensky deposit (Russia) and concentrate of the Zhairemsky GOK (Kazakhstan). The carbothermic reduction was carried out in a sealed resistance furnace (Tamman furnace) with a graphite heater. Ground graphite electrodes were used as a reducing agent. Six corundum crucibles with samples were simultaneously placed in the working space of the furnace. In the first three crucibles, the concentrates of different manganese ores with fraction size range 0.1–0.4 mm and reducing agent in the form of powder were placed. The other three crucibles were filled with the same concentrates of different manganese ores, but without graphite. The furnace was closed with a lid in order to create a reducing atmosphere, heated to temperatures of 900 and 1000 °C and held for 1.5 or 3 hours. The temperature was controlled by a tungsten – rhenium thermocouple W-Re 5/20. The crucibles were cooled down to room temperature with furnace. The resulting reduction products were mechanically separated from the unreacted reducing agent and put into an epoxy resin and polished to make samples with cross sections for analysis. The chemical composition of the phases was determined using an Oxford INCA X – max 80 energy dispersive spectrometer mounted on a JEOL JSM – 7001F scanning electron microscope.

## 4. Results

The structure of ores after reduction at temperature of 900 °C and 1.5 hours reduction time in CO atmosphere is shown in Figure 1, and the chemical composition of the phases at the points of analysis in Table 1. After reduction the metal phase was detected on the surface and inside the ore grains (Figure 1 a, point 3, Figure 1 b, point 3, 4, Table 1). After initial stage of reduction the metal particles contained significant amount of iron. The adjacent oxide phase contained manganese oxides (Figure 1 a, point 1, 2, Figure 1 b, point 1, 2, Figure 1 c, point 1, 2, 3, Table 1), whereas phosphorus remained in the oxide phase during reduction in the atmosphere of CO gas. It should be noted that under these conditions of reduction the metal phases were observed only in the samples of two different types of ore (a and b); in the ore (c), such a change after reduction in the atmosphere of CO was not observed, since this ore contains higher amount of manganese.

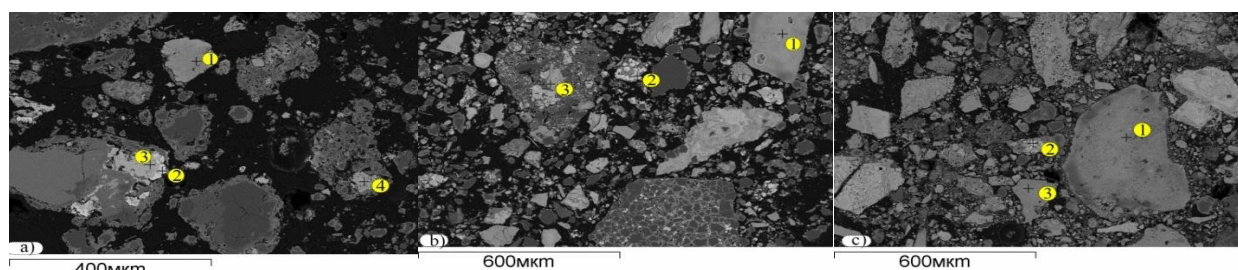
During interaction of ore with solid carbon iron was reduced to a metallic state (Figure 2 a, point 2, 3, Figure 2 b, point 2, Figure 2 c, point 2, Table 2). After reduction the oxide phase of ores mostly contained oxides of manganese, silicon and calcium (Figure 2 a, point 1, Figure 2 b, point 1, 3, Figure 2 c, point 1, 3, Table 2).



**Figure 1.** Reduction by CO at temperature of 900 °C and 1.5 hours reduction time:  
a – manganese concentrate Zhairemsky GOK, b – ferromanganese ore from Selezen deposit  
and c – Brazilian manganese ore.

**Table 1.** The content of elements after recovery, at. %.

Point of analysis	O	Al	Si	P	Mn	Fe	Cu	Ba
Spectrum 1a	26	0.0	1.8	0.0	72.6	0.0	0.0	0.0
Spectrum 2a	11	0.0	0.0	0.0	84.9	0.0	0.0	3.9
Spectrum 3a	0.0	0.0	0.0	0.0	0.0	99.6	0.4	0.0
Spectrum 1b	24	0.0	0.0	0.2	76.3	0.0	0.0	0.0
Spectrum 2b	25	0.0	0.0	0.1	74.5	0.0	0.0	0.0
Spectrum 3b	0.0	0.0	0.0	0.0	0.0	99	1	0.0
Spectrum 4b	0.0	0.0	0.0	0.0	0.0	98.8	0.6	0.0
Spectrum 1c	25	1.3	0.0	0.0	74	0.0	0.0	0.0
Spectrum 2c	30	2.6	0.0	0.0	65.5	2.2	0.0	0.0
Spectrum 3c	29	16.7	1.8	0.0	47.6	4.9	0.0	0.0



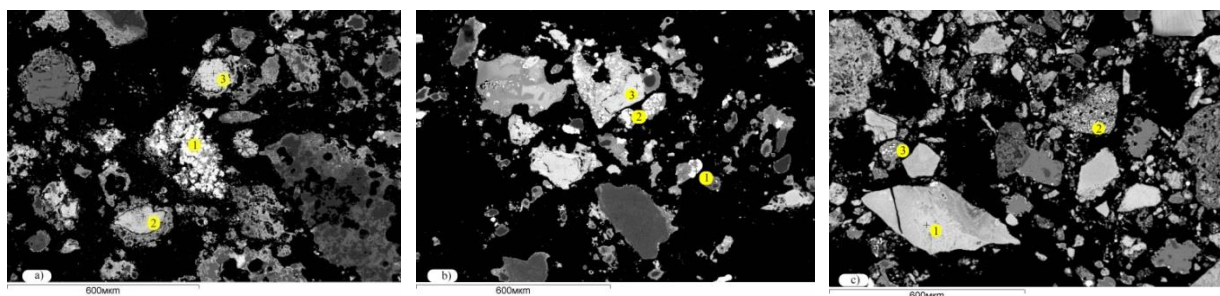
**Figure 2.** Reduction by solid carbon at temperature of 900 °C and 1.5 hours reduction time:  
a – manganese concentrate Zhairemsky GOK, b – ferromanganese ore place of birth Selezen  
and c – Brazilian manganese ore.

**Table 2.** The content of elements after reduction, at. %.

Point of analysis	O	Al	Mn	Fe	Ba	Cu
Spectrum 1a	25	0.0	74.9	0.0	0.0	0.0
Spectrum 2a	0.0	0.0	0.0	100	0.0	0.0
Spectrum 3a	0.0	0.0	3.2	96.8	0.0	0.0
Spectrum 4a	29	0.0	64.6	6.9	0.0	0.0
Spectrum 1b	28	2.3	65.6	0.0	4.1	0.0
Spectrum 2b	0.0	0.0	0.0	99	0.0	1
Spectrum 3b	28	0.0	52.7	17.8	1.5	0.0
Spectrum 1c	28	4.4	63.2	4.5	0.0	0.0
Spectrum 2c	0.0	0.0	0.0	98.5	0.0	1.5
Spectrum 3c	27	3.3	65.9	3.4	0.0	0.0

The experimental results after reduction at temperature of 1000 °C and holding time for 3 hours indicated that iron and phosphorus were reduced in the samples (Figure 3 a, point 1, Figure 3 b, point 1, 2, Figure 3 c, point 3, Table 3). However, under these conditions manganese was also present in

small amounts together with iron in the metal phase. In the oxide phase after reduction by CO, individual phases of manganese monoxide and manganese were found in the silicate phase (Figure 3 a, point 2, 3, Figure 3 b, point 3, Figure 3 c, point 1, 2, Table 3). From the data in Table 3 it follows that in the atmosphere of CO gas in the metal phase the phosphorus content was 0.1–0.4 at. %, that contradicts to the results from Table 1, (Figure 1 a, point 3, Figure 1 b, point 3, 4).

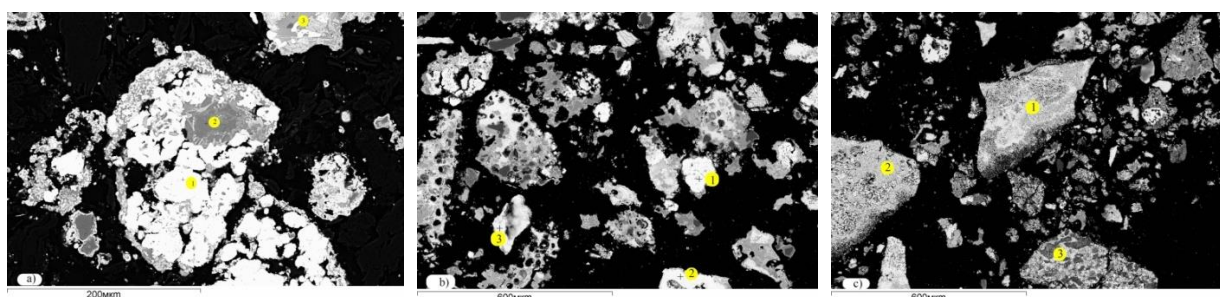


**Figure 3.** Reduction by CO at temperature of 1000 °C and 3 hours reduction time: a – manganese concentrate Zhairemsky GOK, b – ferromanganese ore from Selezen and c – Brazilian manganese ore.

**Table 3.** The content of elements after reduction, at. %.

Point of analysis	O	Al	Si	P	Mn	Fe	Cu	Ba
Spectrum 1a	0.0	0.0	0.0	0.1	0.0	99.9	0.0	0.0
Spectrum 2a	32	0.0	0.0	0.1	61.7	6	0.0	0.0
Spectrum 3a	33	0.0	4.9	0.0	45.4	16.4	0.0	0.0
Spectrum 1b	0.0	0.0	0.0	0.4	0.0	99	0.6	0.0
Spectrum 2b	0.0	0.0	0.0	0.4	8.9	90.5	0.2	0.0
Spectrum 3b	30	1.2	0.0	0.0	64.2	2.1	0.0	3
Spectrum 1c	31	3.6	0.4	0.5	59.2	4.9	0.0	0.0
Spectrum 2c	28	3.9	2.7	0.0	45.4	20	0.0	0.0
Spectrum 3c	0.0	0.0	0.0	0.4	3	95.2	1.4	0.0

At temperature of 1000 °C, the reduction of iron by solid carbon and in the atmosphere of CO occurred in all samples. Metallic iron was formed after reduction, which also contained solution of manganese and phosphorus. It can be seen in (Figure 4 a, point 1, Table 4) that iron was almost completely reduced in contact with solid carbon, and in the samples (b and c) iron was present under these conditions in the oxide phase (Figure 4 b, point 2, 3, Figure 4 c, point 2, 3, Table 4).



**Figure 4.** Reduction by solid carbon at temperature of 1000 °C and 3 hours reduction time: a – manganese concentrate Zhairemsky GOK, b – ferromanganese ore from Selezen and c – Brazilian manganese ore.

**Table 4.** The content of elements after reduction, at. %.

Point of analysis	O	Na	Al	Si	P	K	Mn	Fe	Ba	Cu
Spectrum 1a	0.0	0.0	0.0	0.0	0.1	0.0	0.0	99.9	0.0	0.0
Spectrum 2a	53	2	8.6	27.9	0.0	8.8	0.0	0.0	0.0	0.0
Spectrum 3a	52	1.8	3	29.2	0.0	3.2	6.6	0.0	4.5	0.0
Spectrum 1b	0.0	0.0	0.0	0.0	0.0	0.0	8.9	90.3	0.0	0.8
Spectrum 2b	29	0.0	0.0	0.0	0.0	0.0	62.5	2	6.2	0.0
Spectrum 3b	30	0.0	0.0	0.0	0.1	0.0	63	4	3.1	0.0
Spectrum 1c	31	0.0	0.0	0.0	0.3	0.0	68.5	0.0	0.0	0.0
Spectrum 2c	30	0.0	0.0	0.0	0.0	0.0	67.9	2.1	0.0	0.0
Spectrum 3c	32	0.0	2.9	0.0	0.0	0.0	32.8	32.2	0.0	0.0

## 5. Discussion

The experimental results of solid-phase reduction showed that solid-phase reduction of iron occurred at relatively low temperature (below the melting point of iron and oxide phase). After reduction at temperature of 900 °C and 1.5 hours holding time metallic iron was observed. As the metal phase was reduced in the atmosphere of CO, there were no other elements in the metal. When the temperature was enhanced to 1000 °C, the amount of metallic iron increased, as well as the amount of manganese and phosphorus. With increase in temperature and time of reduction, phosphorus transferred into metal phase together with iron. Thereby, phosphorus was evenly distributed between metal and oxide phases. At temperature of 1000 °C phosphorus transferred into metal despite the type of reducing agent used. In all the experiments, manganese remained in the oxide phase.

## 6. Conclusion

In laboratory conditions, the process of solid-phase selective reduction of iron from various manganese ores was tested in order to determine the possibility of separation of iron and manganese. The experiments confirmed the possibility of iron reduction from complex manganese ores to a metallic state not only by solid carbon, but also CO gas. According to the results of experiments at temperature of 900 °C in the atmosphere of CO gas it is possible to reduce iron selectively from ores (a and b). In the ore (c), such a change was not observed in the atmosphere of CO gas, since this ore contains higher amount of manganese. At temperature of 1000 °C phosphorus transfers into metal despite the type of a reducing agent used. In all the experiments the oxide part mostly contained oxides of manganese, silicon and calcium.

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